Refrigerated multibed adsorption in sampling and analysis of atmospheric light hydrocarbons at ppb (v/v) and sub-ppb (v/v) concentrations

Angels Castellnou[a], Norbert Gonzalez-Flesca[b], Joan O. Grimalt[a,*]

[a]Department of Environmental Chemistry (CID-CSIC), Jordi Girona 18, 08034 Barcelona, Catalonia, Spain
[b]INERIS, Parc Technologique Alata, B.P. 2, 60550 Verneuil-en-Halatte, France

Abstract

Higher ppb (v/v) and sub-ppb (v/v) concentrations of airborne C_2–C_8 light hydrocarbons are obtained when analyzed by refrigerated ($-10°C$) vs. ambient temperature cartridges filled with a combination of carbonaceous packings. The quantitative differences essentially concern some of the lower molecular weight compounds present in higher concentrations, e.g., ethane and propane, as well as toluene. These results have been evidenced from a field comparison involving parallel samplings with both refrigerated and ambient temperature systems and canister collection for reference. The site selected for study is a semi-urban area receiving low traffic pollution inputs. The concentrations provided by these refrigerated tubes are close to those obtained with the canister which is the sampling method giving the highest concentration values in a larger number of compounds. © 1997 Elsevier Science B.V.

Keywords: Air analysis; Sample handling; Volatile organic compounds; Hydrocarbons

1. Introduction

The analysis of trace volatile organic compounds (VOCs) in atmospheric samples generally requires the use of preconcentration systems to overcome low instrumental sensitivity and for sample transport to the laboratory. Among the diverse sampling methods, e.g. solid adsorbents, cryogenic traps, canisters, etc., adsorption onto solid surfaces are those of more common use [1–6]. However, solid adsorbents may involve problems such as analyte breakthrough, incomplete desorption and interferences with artifacts from the adsorbent materials. The combination of various adsorbents in the same sampling cartridge is a useful way to adjust the adsorption and desorp-

tion capacity to the analytes of interest [7,8]. Nevertheless, breakthrough is a serious drawback in many cases, particularly those involving highly volatile species such as light hydrocarbons.

The dependence of breakthrough volumes on analyte and adsorbent properties, concentration levels and other factors have been intensively studied [1,9–11]. However, only limited attention has been devoted to the temperature dependence of the adsorption isotherms, particularly in what concerns practical applications for VOC sampling. The present work is aimed to show that refrigeration of the adsorption cartridges to $-10°C$ during sampling and cryogenic trapping of the ambient water before adsorption provides significant improvements in collection efficiency for the analysis of highly volatile hydrocarbons in the atmosphere. This new

adsorption temperature has been selected based on laboratory tests and practical considerations in view of the technology that can be easily used for field sampling.

The performance of the refrigerated system is evaluated from the analysis of real samples containing light hydrocarbons at sub-ppb (v/v) levels. Simultaneous samplings of refrigerated and ambient temperature cartridges from the same air stream are performed for this purpose. The results are also compared with those obtained with one SUMMA canister used for reference.

2. Experimental

2.1. Sampling equipment and conditioning

The glass cartridges were filled with a multibed system containing 150 mg of Carbotrap C (surface area 10 m^2/g), 150 mg of Carbotrap B (100 m^2/g) and 150 mg of Carbosieve S-III (820 m^2/g), (Supelco, Bellefonte, PA, USA) which are specifically suited to trap VOCs larger than C_8, C_4–C_8 and C_2, respectively [6]. Four cartridges at a time were conditioned by purging with ultra-high-purity helium at 50 ml/min while heated at 350°C for at least 4 h. After conditioning, the sorbent tubes were capped with stainless steel Swagelock nuts and PTFE ferrules and stored until sampling.

The drying tubes (10–12 cm) were composed of stainless steel tubes filled with 830 mg of K_2CO_3 (Prolabo, Normapur, Na free, for analysis, ref. 26727.267; %K_2CO_3, 99–100) equipped with glass wool and a stainless steel frit at each end. These tubes were activated by purging with helium at 50 ml/min while heating at 120°C for 4 h.

Six L Summa electropolished stainless steel canisters were purchased from Andersen Samplers (Atlanta, GA, USA). Cleaning was performed by repetitive evacuation and refilling with humidified zero air while heating at 100°C. Two canisters at a time were handled by introduction in an isothermal oven and connection to a vacuum pump which evacuated the canisters to an absolute pressure of $5 \cdot 10^{-3}$ mbar. A U-shaped open tubular trap cooled with liquid nitrogen was used to prevent contamination from back diffusion of oil from the vacuum pump. The canis-

ters were refilled with humidified zero air until pressure reached 2 bar. Generally this cycle was repeated three times, until no contaminant peaks could be detected by gas chromatographic (GC) analysis.

2.2. Sampling with adsorption tubes

Sampling was performed on a stream of ambient air generated with a stainless steel pipe connected to a high-flow-rate pump (ca. 4 m^3/h). This stream was subsampled with either refrigerated or ambient air tubes using low volume pumps (50 ml/min): 3-l samples were collected in each case.

When refrigerated cartridges were used, moisture was avoided by a cooling trap consisting of an empty glass tube refrigerated at −10°C. The sample portion of the stream air was removed from the manifold through PTFE tubes, drawn into the cooling trap and then into the adsorbent cartridge which was also kept at −10°C in a portable battery-powered freezer during sampling (Fig. 1). This freezer was also used for transport of the samples to the lab in order to maintain −10°C conditions until storage in the laboratory (also at −10°C).

When ambient temperature cartridges were used, the adsorption tubes were connected directly to the pipe holes. In this case, samples were dried in the laboratory using a K_2CO_3 drying tube which was placed in the thermal desorption unit together with a new multibed adsorption cartridge. The sample was then transferred from the initial adsorption cartridge to one of these drying tubes, and then to a new adsorption cartridge. This change prevented the moisture freezing in the cryogenic trap.

2.3. Sampling with canisters

The canisters were evacuated completely before sampling. A pressurized sampling system, Andersen Model 87-200 Volatile Organic Compound Canister Sampler (VOCCS), was used to draw ambient air from the sampling manifold and to fill and pressurize the canister. A discharge port on the rear of the instrument cabinet vented the unsampled air. A small portion of this sample air was removed from the manifold by a modified inert diaphragm vacuum pump in conjunction with an electronic mass flow
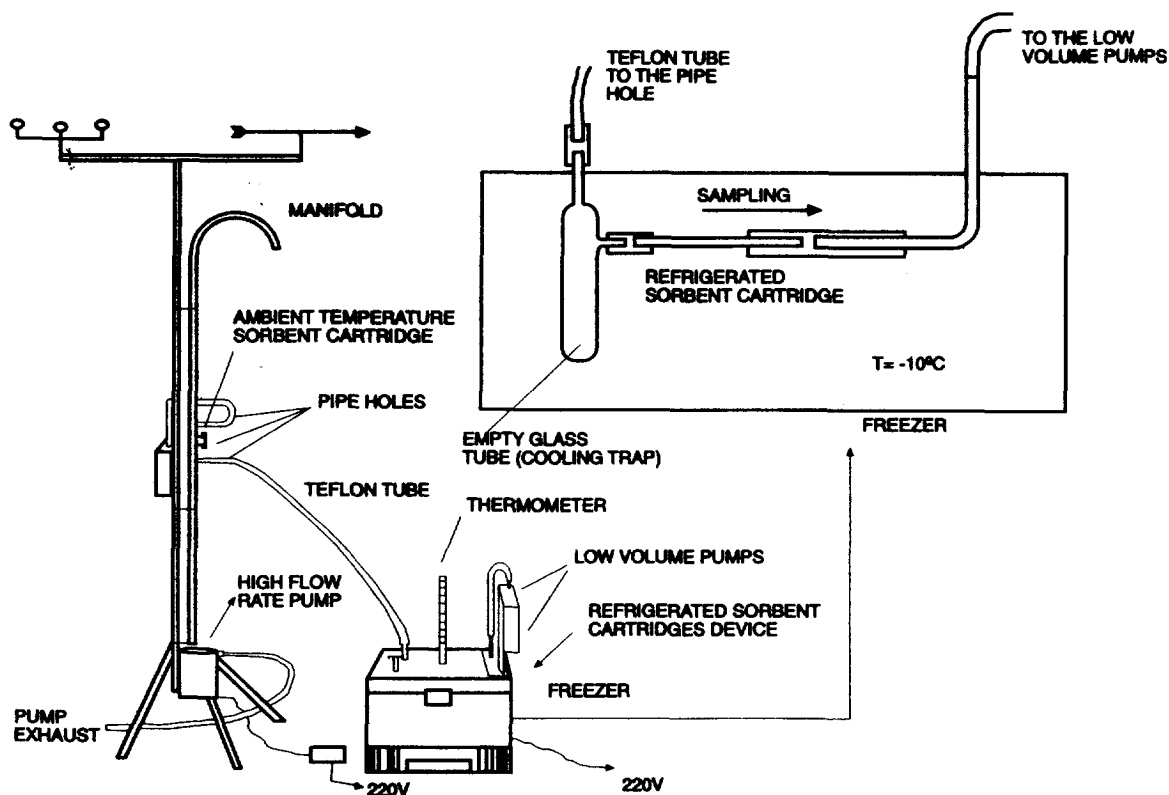
Fig. 1. Diagram showing the setting for the joint sampling with ambient temperature and refrigerated (−10°C) adsorption tubes.

controller. The flow controller device maintained a constant flow (about 30 ml/min) into the canister over the fixed sampling period (about 10 h) until the target pressure in the canister was achieved (about 20–25 p.s.i.; 1 p.s.i.=6894.76 Pa). A digital timer was used to preselect sampling periods, start and stop times.

After sample collection, the VOC were measured in the laboratory by transfer of a known volume of air in the canister (ca. 1.5 l) to a K_2CO_3 drying tube serially connected to a multibed glass cartridge (30 ml/min). The drying tubes were replaced every two samples. The air volume and flow were controlled by a flow and a volume meter connected after the cartridge.

2.4. Instrumental analysis

Analyses were performed with a Fisons Model 8000 GC (Rodano, Italy) equipped with a thermal desorption unit (Dynatherm, Supelco) and a conventional flame ionization detection (FID) system. The desorption system was a Model 850 Thermal Desorber Envirochem (Supelco) coupled to a cryofocussing device Model MFA 815 Cold Trap (Fisons, Rodano, Italy). This cryofocussing unit was a 0.53-mm I.D. fused-silica capillary tube cooled with liquid nitrogen to −150°C. VOCs were desorbed at 300°C for 5 min at a flow-rate of 44 ml/min. Then, they were refocussed on the cryogenic unit and the sample was rapidly desorbed at 300°C within 35 s into the gas chromatographic column. Separation was performed on a 30-m×0.53-mm I.D. porous layer open tubular column coated with aluminum oxide and deactivated with potassium chloride (film thickness 10 μm, Chrompack, Middelburg, The Netherlands). The oven of the chromatograph was programmed from 30°C (holding time 7 min) to 180°C at 6°C/min with a final holding time of 33 min.

Compound identification was performed with GC coupled to a mass spectrometer Fisons MD-800. Known volumes of these standards were introduced directly into the thermal desorber and were analysed as described above.

2.5. Calibration and quantitation

Quantitation was performed using hydrocarbon gas standards from Scott Specialty Gases (Durham, NC, USA): mixtures, ref. nos. 2-3470, 2-3444, 2-3471 and 2-3445, were used. Volumes (0.5 ml) were taken with gas-tight syringes and directly introduced into the thermal desorber unit.

About 1 ml of these reference mixtures was also introduced into the canisters that were subsequently pressurized to 2 bar with helium. These canisters were then analyzed as described above. Linearity was checked taking variable volumes of these mixtures.

Finally, a dynamic atmosphere unit [11] was also used to generate air mixtures of known composition, which were analyzed to certify the accuracy of the measurements.

3. Results and discussion

3.1. Test site and samples

The site selected for study was Marignane, a semirural area situated near Etang de Berre, a coastal pond located in the so-called Fos-Berre region (South of France). The region is well known for its important industrial concentration and large vehicle fleet. The samples described in this comparison were taken on 29 September 1994 in a relatively low polluted site. Parallel measurements using one canister and multibed adsorption cartridges were performed. An integrated sample of ca. 18 l was obtained with the canister. The adsorption tubes were used continuously and replaced every 2 h, providing parallel samples of 3 l in each case. The canister sampler and the stainless-steel pipes for the cartridges were placed at about 15 m from the lake.

The canister sample was taken as reference in the comparison of the ambient temperature and refriger-ated adsorption cartridges. Canisters have shown to be successful for VOC measurements in the analysis of halocarbons [from ppb (v/v) (ppbv) [12] to ppt (v/v) (pptv) [4,13,14] levels], C_2–C_{10} VOCs (down to the subparts-per-bilion range [15]), polar VOCs (at ppbv levels [16]) and non-polar toxics from hazard-ous waste incineration [17]. A comprehensive study on the applicability of canisters to a large number of volatile organic compounds at ppbv levels has recently been reported [18]. The performance of passivated canisters has also shown to be successful when compared with direct VOC measurement with GC [19] or Fourier transform infrared spectrometry [20].

3.2. Volatile hydrocarbons: qualitative composition

Representative chromatograms of the ambient air samples collected at Marignane with the canister and the refrigerated and ambient temperature cartridges are shown in Fig. 2. The aluminum oxide columns provide high resolution for the separation of light hydrocarbons without the need for subambient oven temperatures in the chromatograph. Thus, baseline separations of linear, cyclo- and isoalkanes, e.g. cyclo-, n- and isobutane, but-1-ene and pentane, are achieved. The profiles displayed in Fig. 2 do not exhibit differences in qualitative composition. Thus, the diverse systems of sampling and elimination of humidity considered in this study do not involve loss or severe discrimination of the airborne compounds amenable to analysis with aluminum oxide capillary columns.

Some of the compounds encountered are not originally present in gasolines, particularly the un-saturated compounds such as ethene and propene [21]. These hydrocarbons are formed as a conse-quence of vehicle combustion processes and emitted by the engine exhausts [21–23]. However, the ratios between unsaturated and saturated species in these samples, e.g. ethene/ethane and propene/propane, are considerably lower than those found in vehicle exhaust [21–23]. This difference and the very low amount of acetylene in the Marignane samples shows that the sampled hydrocarbons correspond to vehicle exhaust mixtures that have undergone some degree of degradation, namely photooxidation.
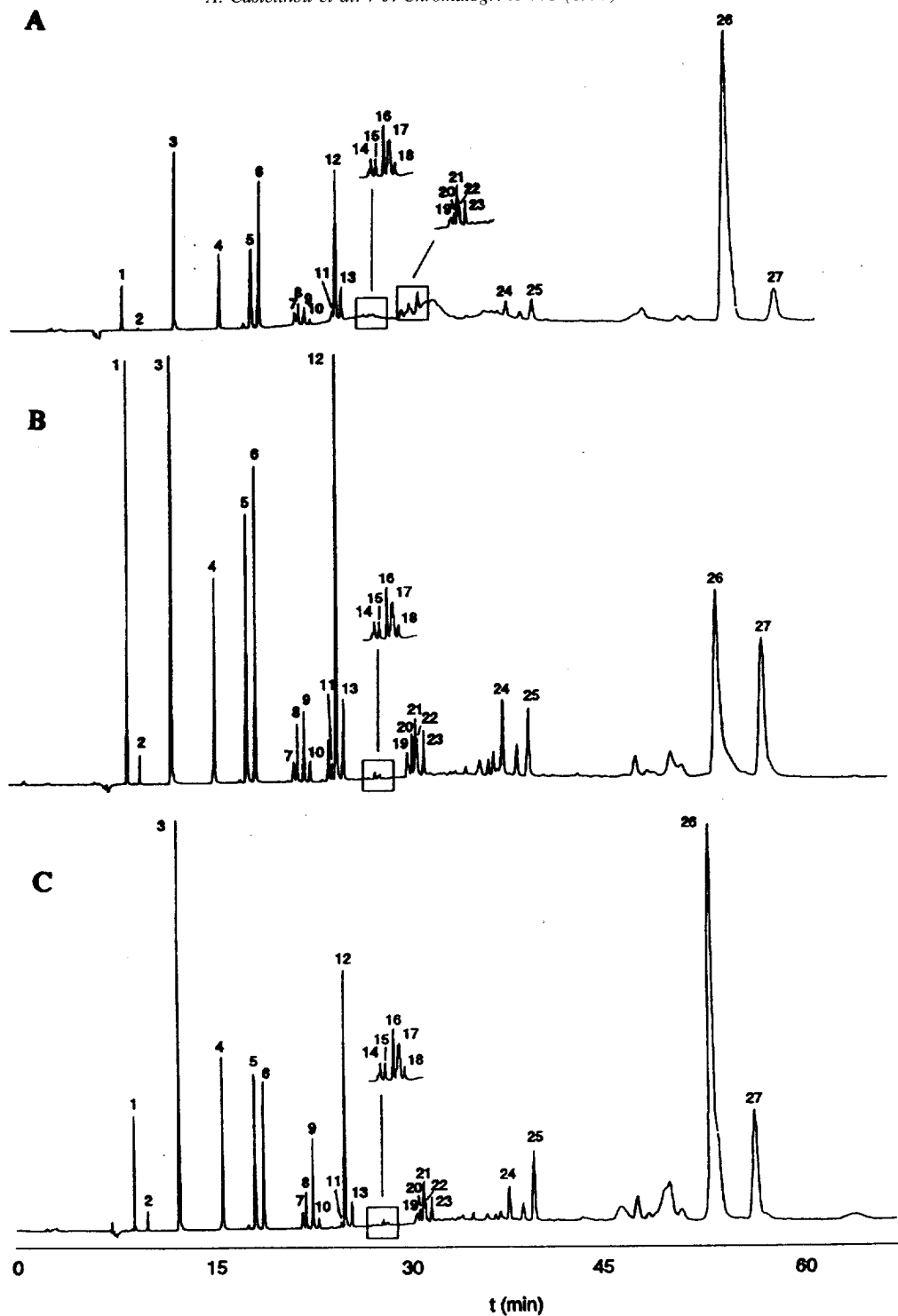
Fig. 2. Representative chromatograms of an ambient air sample collected with canister (A), refrigerated (−10°C) (B), and ambient temperature (C) multibed adsorption cartridges. Peak numbers refer to Table 1. Note that the canister and the cartridge samples correspond to 1.5 and 3 l of air, respectively.

3.3. Quantitative composition

The quantitative results obtained with the different sampling systems are summarized in Table 1. The measured concentrations are low, typical of sub-ppbv background levels in areas with relatively low vehicular traffic inputs [24,25]. As described above, the canister provided time-integrated data whereas tube collection, either ambient temperature or refrigerated, corresponds to 2-h periods. A problem of contamination with *n*-octane in the canisters prevented this compound from being included in the comparison. No problems of interferences or artifacts have been observed with the adsorption cartridges.

The refrigerated cartridges give higher VOC concentrations than the ambient temperature tubes in almost all cases. The only exception is represented by *cis*- and *trans*-but-2-ene which exhibit the same airborne levels for the two types of tubes. The concentrations provided by the refrigerated tubes are closer to those observed in the canister which is the method giving the highest values in a larger number of compounds.

A detailed comparison of the differences between the concentrations obtained with the ambient and refrigerated cartridges and the canister is represented in Fig. 3. The refrigerated tubes and canister exhibit similar values. In contrast, the ambient temperature tubes show significantly lower concentrations than the canister, particularly in the case of the lower-molecular-mass compounds present in high concentrations. Thus, a considerable increase in sampling

Table 1

Volatile organic compounds obtained from the parallel sampling of refrigerated and ambient temperature multibed adsorption cartridges

Compound	Canister	Refrigerated tubes (mean)	Ambient temperature tubes (mean)
1 Ethane	1	1±0.7[a]	0.3±0.1
2 Ethylene	0.3	0.3±0.3	0.2±0.2
3 Propane	4	3±2	2±0.7
4 Propene	1	0.7±0.6	0.4±0.2
5 Isobutane	2	1±0.7	0.7±0.2
6 *n*-Butane	3	2±0.8	1±0.5
7 *trans*-But-2-ene	0.4	0.2±0.03	0.2±0.07
8 *n*-But-1-ene	0.4	0.3±0.2	0.2±0.06
9 Isobut-1-ene	0.6	0.5±0.1	0.3±0.1
10 *cis*-But-2-ene	0.1	0.1±0.07	0.1±0.05
11 Cyclopentane	0.2	0.1±0.09	0.08±0.02
12 Isopentane	3	3±1	2±0.6
13 *n*-Pentane	0.8	0.7±0.2	0.4±0.2
14 *trans*-Pent-2-ene	0.02	0.05±0.04	0.02±0.01
15 2-Methylbut-2-ene	0.04	0.03±0.03	0.02±0.01
16 *n*-Pent-1-ene	0.05	0.09±0.07	0.06±0.03
17 2-Methylbut-1-ene	0.08	0.1±0.1	0.05±0.02
18 *cis*-Pent-2-ene	0.03	0.02±0.02	0.01±0.01
19 2,2-Dimethylbutane	0.2	0.2±0.2	0.1±0.04
20 Cyclohexane	0.07	0.3±0.2	0.06±0.02
21 2-Methylpentane	0.2	0.2±0.1	0.2±0.08
22 3-Methylpentane	0.1	0.1±0.07	0.1±0.05
23 *n*-Hexane	0.4	0.2±0.07	0.2±0.05
24 2,3-Dimethylpentane	0.7	0.8±0.5	0.5±0.2
25 Benzene	1.0	0.8±0.1	0.8±0.2
26 *n*-Octane	20[b]	5±3	4±2
27 Toluene	3	3±2	2±0.5

The concentrations obtained with one canister operating during the whole collection period are given for reference. Concentrations in ppbv.
[a] The mean interval is defined as $t\sigma_{n-1}/\sqrt{N}$, where t is the Student statistics for $\alpha=0.05$, σ is the standard deviation and N the number of replicates (five for the refrigerated tubes and 10 for the ambient temperature tubes).
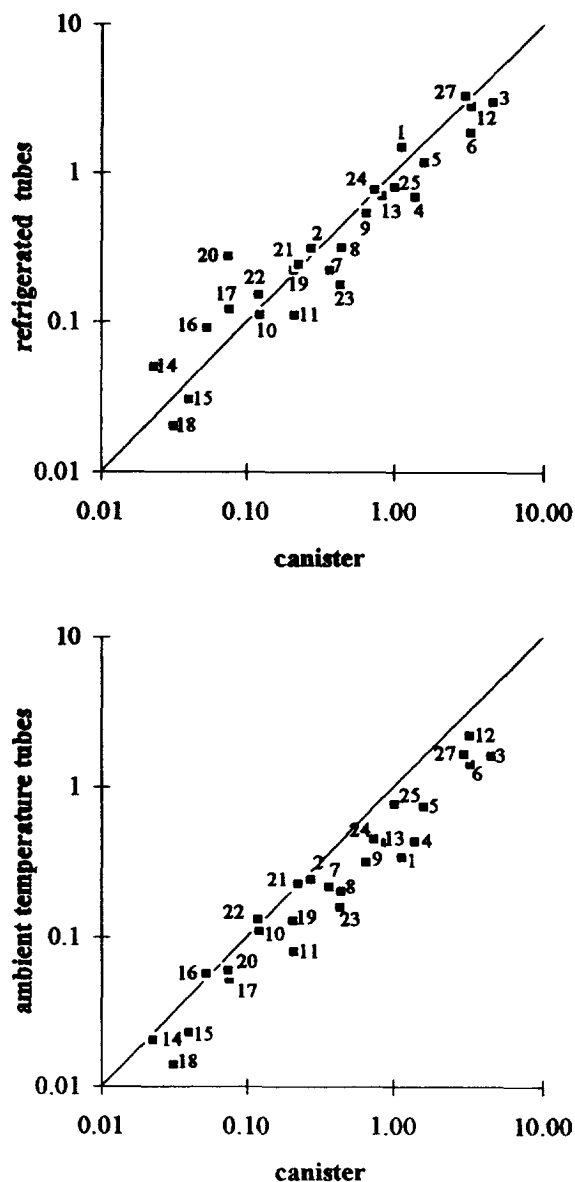[b] Measurement influenced by external contamination.

The relationship between retention values and temperature of the adsorbed compounds can be linearized when representing log V_N vs. $1/T$, where V_N is the retention volume and T the temperature in absolute degrees [2,26–28]. The slope of these plots provides an indication of the differential adsorption energy of the compound (ΔU):

$$\Delta U = -R \cdot \{(d \ln V_N)/[d(1/T)]\} \qquad (1)$$

These plots parallel the well-known graphs that linearize the relationship between vapour pressure (P) and temperature in which the slope is determined by the molar enthalpy of vaporization (ΔH):

$$\Delta H = -R \cdot (d \ln P)/[d(1/T)] \qquad (2)$$

ΔU has been reported to be constant over temperatures down to 20°C. In view of the results of the present study, the linearity of the log V_N vs. $1/T$ plots at lower temperatures should be tested. However, this task is beyond the scope of the present paper.

3.4. Water elimination at desorption

Since water was eliminated in all sampling processes considered in the present study, the differences described in Table 1 and Fig. 3 cannot be attributed to differences in breakthrough volumes due to humidity [29]. Furthermore, these differences cannot be due to the methods chosen for elimination of the water retained in the adsorption cartridges since the same system, adsorption on K_2CO_3 tubes, is used for the ambient temperature tubes and the canister. This method provides efficient removal of sample humidity from the mixtures of atmospheric highly volatile hydrocarbons without interferences from organic materials. These adsorption tubes can be easily re-conditioned and tested for organic contamination and sample memory effects. Prior to the present study, the canisters were used to perform various tests on the possible adsorption effects of K_2CO_3. No analyte adsorption was observed, which is in agreement with the tests performed in other studies [14].

Humidity is, in fact, a critical aspect for the aluminum oxide chromatographic columns, which may show significant retention time changes as consequence of the adsorption of polar molecules,

Fig. 3. Comparison of the VOC concentrations obtained with canister (integrated sample ca. 18 l) and those obtained with refrigerated and ambient temperature multibed adsorption cartridges (3 l), sampling in parallel in one site of moderate pollution. The straight line indicates a slope = 1 (the same composition of canister and cartridges at any concentration). Peak numbers refer to Table 1. Note that the scale axis are logarithmic.

efficiency is obtained by cooling the adsorption cartridges at −10°C during sampling and cryogenic trapping of the ambient water before adsorption.

such as water on the active aluminum oxide layers. Humidity excess may even cause column blockage or other problems such as flame extinction in the FID system or overpressurization in the mass spectrometer. Changes in detector response may also be encountered as a consequence of humidity. In this respect, the use of K_2CO_3 tubes represents an efficient solution for water elimination because these tubes can be easily re-conditioned and tested for organic contamination and sample memory effects. Other methods commonly used for this purpose, e.g. permeable membrane dryers [30,31] may introduce contaminants which interfere with the compounds to be determined in the samples, namely isobut-1-ene, benzene and toluene [32].

However, in the case of the refrigerated adsorption cartridges, the use of these drying K_2CO_3 tubes is not necessary because the refrigeration system can be used to create a cryogenic trap for humidity, as described in the experimental section. This cryogenic trap is an additional advantage of the refrigerated system that simplifies both the instrumental set-up and sample handling. Thus, besides the modification of the adsorption isotherms due to the temperature change, this refrigerated system allows to eliminate the competitive effect of the water molecules for the adsorption sites which further enhances adsorption of VOCs.

4. Conclusions

The cartridges refrigerated at $-10°C$ give higher concentrations than the ambient temperature tubes in practically all atmospheric light hydrocarbons analyzed. The highest differences between the two methods concern some of the lower-molecular-mass hydrocarbons in higher concentrations, such as ethane and propane, as well as toluene. The concentrations provided by these refrigerated tubes are close to those obtained with the canister which is the sampling method giving the highest concentration values in a larger number of hydrocarbons.

Acknowledgments

References

[1] L.D. Butler, M.F. Burke, J. Chromatogr. Sci. 14 (1976) 117–122.

[2] R.H. Brown, C.J. Purnell, J. Chromatogr. 178 (1979) 79–90.

[3] J. Namiesnik, L. Torres, E. Kozlowski, J. Mathieu, J. Chromatogr. 208 (1981) 239–252.

[4] J. Rudolph, K.P. Müller, R. Koppmann, Anal. Chim. Acta 236 (1990) 197–211.

[5] X.-L. Cao, C.N. Hewitt, J. Chromatogr. A 710 (1995) 39–50.

[6] V. Camel, M. Caude, J. Chromatogr. A 710 (1995) 3–19.

[7] D. Helmig, J.P. Greenberg, J. Chromatogr. A 677 (1994) 123–132.

[8] K.D. Oliver, J.R. Adams Jr., E.H. Daughtrey, W.A. McClenny, M.J. Yoong, M.A. Pardee, E.B. Almasi, N.A. Kirshen, Environ. Sci. Technol. 30 (1996) 1939–1945.

[9] F.R. Cropper, S. Kaminsky, Anal. Chem. 35 (1963) 735–743.

[10] J. Russell, Environ. Sci. Technol. 9 (1975) 1175–1178.

[11] P. Comes, N. Gonzalez-Flesca, T. Menard, J.O. Grimalt, Anal. Chem. 65 (1993) 1048–1053.

[12] K.D. Oliver, J.D. Pleil, W.A. McClenny, Atmos. Environ. 20 (1986) 1403–1411.

[13] D.E. Harsch, Atmos. Environ. 14 (1980) 1105–1107.

[14] S. Müller, M. Oehme, J. High Resolut. Chromatogr. 13 (1990) 34–39.

[15] C.T. Farmer, P.J. Milne, D.D. Riemer, R.G. Zika, Environ. Sci. Technol. 28 (1994) 238–245.

[16] T.J. Kelly, P.J. Callahan, J. Pleil, G.F. Evans, Environ. Sci. Technol. 27 (1993) 1146–1153.

[17] A.R. Gholson, J.F. Storm, R.K.M. Jayanty, R.G. Furest, T.J. Logan, M.R. Midgett, J. Air Pollut. Control Assoc. 39 (1989) 1210–1217.

[18] D.A. Brymer, L.D. Ogle, C.J. Jones, D.L. Lewis, Environ. Sci. Technol. 30 (1996) 1188–1195.

[19] R.E. Berckley, J.L. Varns, J. Pleil, Environ. Sci. Technol. 25 (1991) 1439–1444.

[20] R.E. Carter Jr., M.J. Thomas, G.A. Marotz, D.D. Lane, J.L. Huson, Environ. Sci. Technol. 26 (1992) 2175–2181.

[21] R.A. Harley, M.P. Hannigan, G.R. Cass, Environ. Sci. Technol. 26 (1992) 2395–2408.

[22] J.C. Bailey, B. Schmidl, M.L. Williams, Atmos. Environ. 24 (1990) 43–52.

[23] D. Gaudioso, R. Vaccaro, S. Brini, M.C. Cirillo, C. Trozzi, Ing. Ambient. 20 (1991) 244–251.

[24] R.G. Derwent, D.R. Middleton, R.A. Field, M.E. Goldstone, J.N. Lester, R. Perry, Atmos. Environ. 29 (1995) 923–946.

[25] A. Rosell, J.O. Grimalt, M.G. Rosell, X. Guardino, J. Albaiges, Fresenius J. Anal. Chem. 339 (1991) 689–698.

[26] A. Raymond, G. Guiochon, J. Chromatogr. Sci. 13 (1975) 173–177.

[27] L.D. Butler, M.F. Burke, J. Chromatogr. Sci. 14 (1976) 117–122.

[28] C. Vidal-Madjar, M.-F. Gonnord, F. Benchah, G. Guiochon, J. Chromatogr. Sci. 16 (1978) 190–196.

[29] G.O. Wood, Am. Ind. Hyg. Assoc. J. 48 (1987) 622–625.

[30] J.F. Pankow, Environ. Sci. Technol. 25 (1991) 123–126.

[31] W.A. McClenny, K.D. Oliver, E. Hunter Daughtrey Jr., J. Air Waste Manag. Assoc. 45 (1995) 792–800.

[32] H. Boudrier, Ph.D. Thesis, Université Paris VII, 1994.