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Effect of addition of a graphitized carbon black trap to a glass beads trap on the cryoconcentration of some non-methane hydrocarbons in ambient air

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Abstract

Carbotrap was added to a glass beads cryotrap in order to increase the retention of the very volatile two-carbon hydrocarbons, ethylene, ethane and acetylene. Indeed the obtained recoveries increased from 2 to 3% for ethylene, the poorest retained compound, from 7 to 20% for ethane and from 23 to 31% for acetylene between the glass beads only and the Carbotrap/glass beads cryotrap. The addition of the Carbotrap, however, decreased the obtained recovery of *o*-xylene by 22–46%, depending on the employed conditions. The smaller decrease was observed when the longer desorption time was employed. The variation of the temperature of desorption by 40°C had very little effect on the resulting recoveries. © 1997 Elsevier Science B.V.

Keywords: Cryogenic trapping; Air analysis; Sample handling; Graphitized carbon black; Glass beads; Environmental analysis; Volatile organic compounds; Ethylene; Ethane; Acetylene; Xylenes

1. Introduction

The C₂–C₁₀ hydrocarbons in ambient air, anthropogenic and biogenic, are established precursors of ozone formation. The qualitative and quantitative determination of the C₂–C₁₀ non-methane hydrocarbons, NMHCs, is required knowledge for the validation of photochemical models, developed for the abatement of photochemical pollution.

The most common analytical method employed for the determination of ambient air C₂–C₁₀ NMHCs is gas chromatography–flame ionization detection (GC–FID) or mass spectrometry (MS). However, the detection limits of these methods are usually

higher than the atmospheric concentrations of NMHCs and thus a concentration of the air sample is required. The concentration of the more volatile C₂ hydrocarbons is very demanding. All commercially available units, nowadays, use two-stage concentration procedures. In the first stage ambient air is concentrated in traps of length around 25 cm×1/8 in. O.D. (1 in.=2.54 cm) filled with adsorbents and operated at ambient (Xon Tech [1]), or subambient (Chrompack [2,3]; Xon Tech [1]) temperatures. Glass beads have also been used extensively as a packing material of the concentration trap. Their advantage is their superior inactivity towards the sampled hydrocarbons, at the high temperatures used in desorption. It was shown that when only glass beads are used in the concentration trap a tempera-

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ture as low as -194°C must be employed for the collection of the C_2 hydrocarbons [4]. However, only Graseby/Nutech has reported manufacturing of units that can attain temperatures as low as -196°C . Entech's cryoconcentrator operates at -180°C , so that to effectively collect the C_2 hydrocarbons they added an adsorbent to the glass beads trap [5]. Some laboratory-made cryoconcentration units have been reported to operate at -186°C to -196°C [6–8]. All commercial units in addition employ a second stage, a cryofocuser, where the concentrated (in the first stage) sample is further reduced in size by cryocollection on the capillary column (it maybe the analytical or a separate capillary) in order to improve the resolution of the analytical capillary column. Thus, Xon Tech cools the cryofocuser at -185°C [1]; Nutech cools the cryofocuser at -196°C ; Entech at -185°C [5] and Chrompack cools 20 cm of capillary filled with $\text{Al}_2\text{O}_3/\text{KCl}$ at -150°C [2].

The minimum temperature that our concentrator unit, manufactured by Tekmar, can attain is -180°C at both stages (cryoconcentration and cryofocusing). Thus, it was not possible to concentrate the C_2 hydrocarbons, and particularly ethane and ethylene, on glass beads [9]. For this reason we replaced a portion of glass beads with an adsorbent. The adsorbent selected was Carbotrap, a graphitized carbon black available from Supelco. It is recommended to be used for trapping C_4 – C_8 compounds at ambient temperature [10]. This compound was selected because it has been reported in the literature as being used in traps for collecting hydrocarbons from ambient air [1–3,11].

In the present work we examine the effect of the replacement of a portion of glass beads trap with Carbotrap, on the retention of the very volatile C_2 hydrocarbons and on the desorption of *o*-xylene, a less volatile constituent of ambient air and compare the results with those obtained from a cryotrap containing only glass beads.

2. Experimental

Ethane, ethylene and acetylene were the very volatile studied hydrocarbons. A nominal 11 ppmv (parts per million, v/v) single hydrocarbon mixture was prepared by addition of the appropriate volume

of the pure hydrocarbon, obtained from Messer Griesheim (Düsseldorf, Germany), to a 4.5-l glass flask, evacuated and filled with air purified by an Aadco unit (Clearwater, FL, USA). The *o*-xylene gaseous solution was prepared by injecting, to the line filling the 4.5-l flask with air, the appropriate amount of liquid *o*-xylene, Aldrich HPLC grade (Milwaukee, WI, USA), to make a final concentration of 22.2 ppm. 1 ml of ethane, ethylene, acetylene and *o*-xylene mixtures, were injected with Precision Sampling (Baton Rouge, LA, USA) gas-tight syringes to a Tekmar 5010 GT Thermal Desorber (Cincinnati, OH, USA), modified in the laboratory by the addition of an injection port to the flow line loading the cryotrap and redirection of the plumbing to eliminate the room temperature adsorption trap. The injected quantities are equal to those resulting from a 1-l sample of concentration several ppbv. The flow of helium, 10 ml/min, loading the sample, was maintained for 5 min to ensure the loading of the trap.

The cryoconcentration traps, cryo-1, Fig. 1, were stainless-steel tubes, 20 cm \times 1/8 in. O.D.. One was filled with unsilanized glass beads 60–80 mesh (Tekmar) and the second with Carbotrap 20–40 mesh (Supelco, Bellefonte, PA, USA) (10 cm) and glass beads 60–80 mesh (10 cm). Cryo-1 could be cooled to -180°C ($\pm 5^{\circ}\text{C}$) and flash heated at a rate of $10^{\circ}\text{C}/\text{s}$ up to 300°C . Prior to desorption cryo-1 was purged with helium in order to remove possible remaining oxygen. In the desorption mode cryo-1 was backflushed with the desorbing gas to the cryofocuser, cryo-2. Cryofocusing was performed by cooling to -180°C ($\pm 5^{\circ}\text{C}$) (the minimum possible

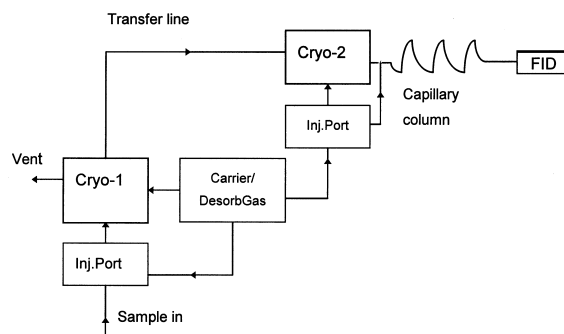


Fig. 1. Flow diagram of concentration system.

temperature) approximately 8 cm of the analytical column and flash heating it at a rate of 8.3°C/s up to 300°C. The 8-port switching valve was heated at 280°C and the 0.32 mm I.D. capillary aluminum clad silica transfer line connecting cryo-1 with cryo-2 at 270°C. As shown in Fig. 1, our unit is equipped with one injection port-1, where injected samples are directed to cryo-1 and the packed injection port of the chromatograph, where the injected samples are directed to cryo-2.

The Tekmar unit was interfaced to a Hewlett-Packard 5890 Series II gas chromatograph equipped with an FID system set at 280°C. In the experiments carried out for the determination of the collection efficiency of the cryofocuser 0.5 ml sample was injected in the packed injection port heated at 270°C. The analytical column was a HP-1, 50 m×0.32 mm I.D. and 1.05 µm film thickness, non-polar 100% methyl silicone gum capillary column. For the separation of ethane, ethylene and acetylene the following program used was: initial temperature -40°C for 1 min, rate of 3°C/min up to 140°C and at 30°C/min up to 230°C. For the analysis of *o*-xylene the initial temperature was 80°C, then rate of 3°C/min up to 140°C and at 30°C/min up to 230°C.

A blank run (run without the addition of analyte) was always performed prior to an analysis. If the obtained analyte values were less than 0.01 of the expected sample values we proceeded with the analysis. If not, the cryotrap was heated at 40°C with desorb gas at 10 ml/min for time periods of 30–60 min, as many times as required, until the analyte values fulfilled the above criterion. Additional cleaning of the cryotrap was performed by heating it at 290°C and using the desorb gas to carry the impurities away through the column.

3. Results and discussion

For ethane, ethylene and acetylene, the most volatile of the NMHCs, efforts were directed to ensure complete retention. The factors that determine full retention, and which we could vary, were the sampling (loading) flow-rate, the temperature and the packing material of the cryo-1.

With the glass beads cryo-1 and cryo-2 cooled to -180°C, ethylene yielded a recovery of 2% at 10

ml/min loading flow-rate and 6% at flow-rate 2 ml/min. At loading flow-rate 10 ml/min, ethane yielded a recovery of 7% and acetylene 23%. Recovery, expressed as percent, is the amount determined from the cryoconcentration procedure divided by the amount determined from the direct injection to the analytical column.

With the Carbotrap/glass beads cryo-1 and cryo-2 set at the minimum possible temperature of -180°C ($\pm 5^\circ\text{C}$), the recoveries increased and thus the effect of the sampling flow-rate on the retention on the cryotrap was examined. The results are shown in Fig. 2. Three sampling flow-rates were examined 2, 5 and 10 ml/min. Although the highest possible sampling rate is desired, because of smaller analyses times and less cryogen consumption, a faster flow-rate was not

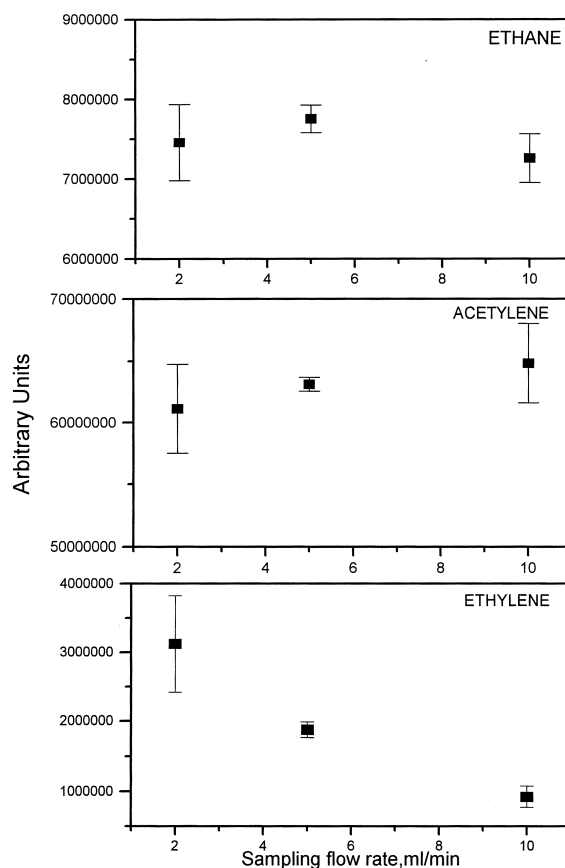


Fig. 2. Effect of sampling (loading) flow-rate on the obtained detectors signal for ethane, acetylene and ethylene. Cryo-1 used Carbotrap/glass beads.

meaningful because, as shown in Fig. 2, ethylene's retention decreased from 2 to 5 and even more so at 10 ml/min. The recovery of ethylene was 9 and 3% at flow-rates 2 and 10 ml/min, respectively. Acetylene and ethane were better retained, with recoveries of 31 and 20%, respectively, irrespective of sampling flow-rate. The recoveries presented above are due to the sum of retention by cryo-1 and cryo-2, that is breakthrough is possible in both steps. However, the recoveries using only the cryo-2 were determined in separate experiments by injecting the same volume of sample to injection port-2 with and without the use of cryo-2. Recoveries for acetylene, ethane and ethylene were 97, 88 and 70%, respectively. These results indicate that for acetylene and ethane practically all breakthrough occurred at cryo-1, whereas for ethylene a significant amount was also lost at cryo-2.

The two traps were also tested with ambient air samples, collected in Summa passivated canisters obtained from BRC-Rasmussen. The results, as shown in Figs. 3 and 4 of the relevant portions of the

chromatograms, were the same as with the laboratory samples. The Carbotrap/glass beads trap retained the C₂ hydrocarbons more efficiently.

The conditions determined for the C₂ hydrocarbons are also applicable to the other hydrocarbons contained in the ambient air samples together with ethane, ethylene and acetylene. The recovery of *o*-xylene, a C₈ hydrocarbon, was examined under the conditions set for the very volatile hydrocarbons; *o*-xylene is an important ambient air hydrocarbon and the reported results may pertain to the other similarly volatile hydrocarbons.

The factors that determine complete desorption from a cryotrap, and which we could vary, were the temperature at which the trap is heated, the desorption time and the flow-rate of the desorbing gas. All these factors vary with the adsorbent used. The variation of the flow-rate of the helium desorbing gas is a very cumbersome procedure with our unit, because it also changes the column carrier gas flow-rate. For this reason in all experiments the transfer, from cryo-1 to cryo-2, flow-rate was 1.5 ml/min.

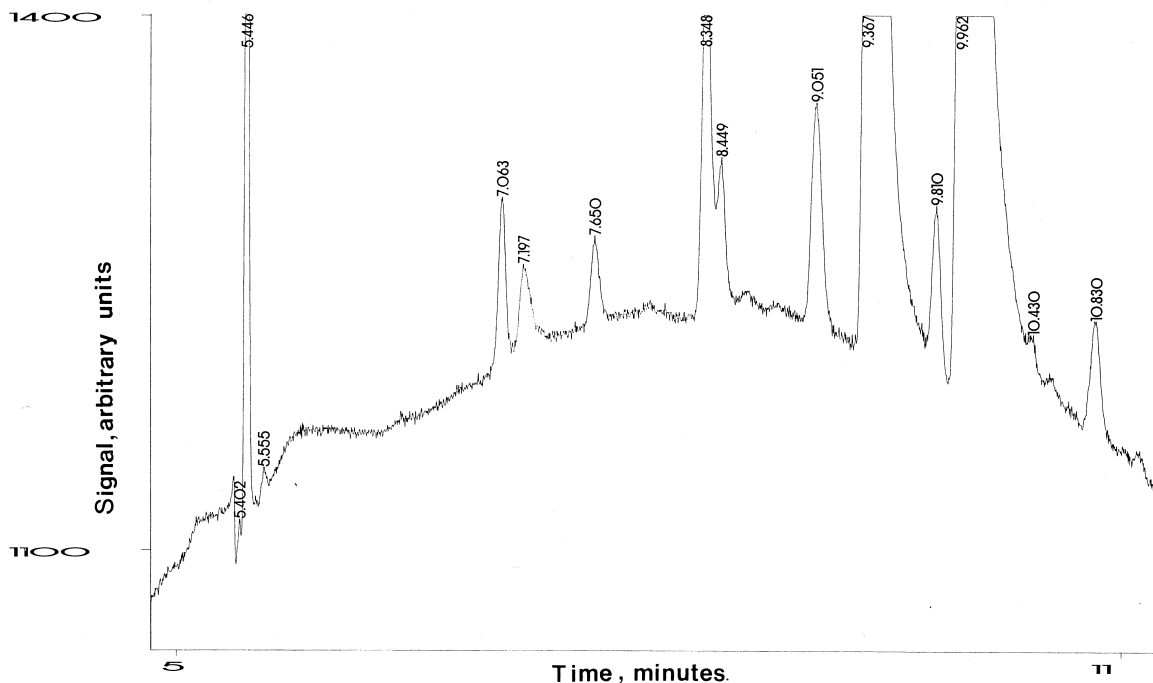


Fig. 3. Relevant portion of ambient air chromatogram, obtained after cryoconcentration on filled with glass beads only cryo-1. Elution times: ethene: 5.402, acetylene: 5.446, ethane: 5.555, propene: 7.063, propane: 7.197, isobutane: 9.051, isobutene and butene-1: 9.810, *n*-butane: 9.962, *trans*-butene-2: 10.430, *cis*-butene-2: 10.830. A Nafion dryer was used for the removal of moisture from a 1.5-l sample.

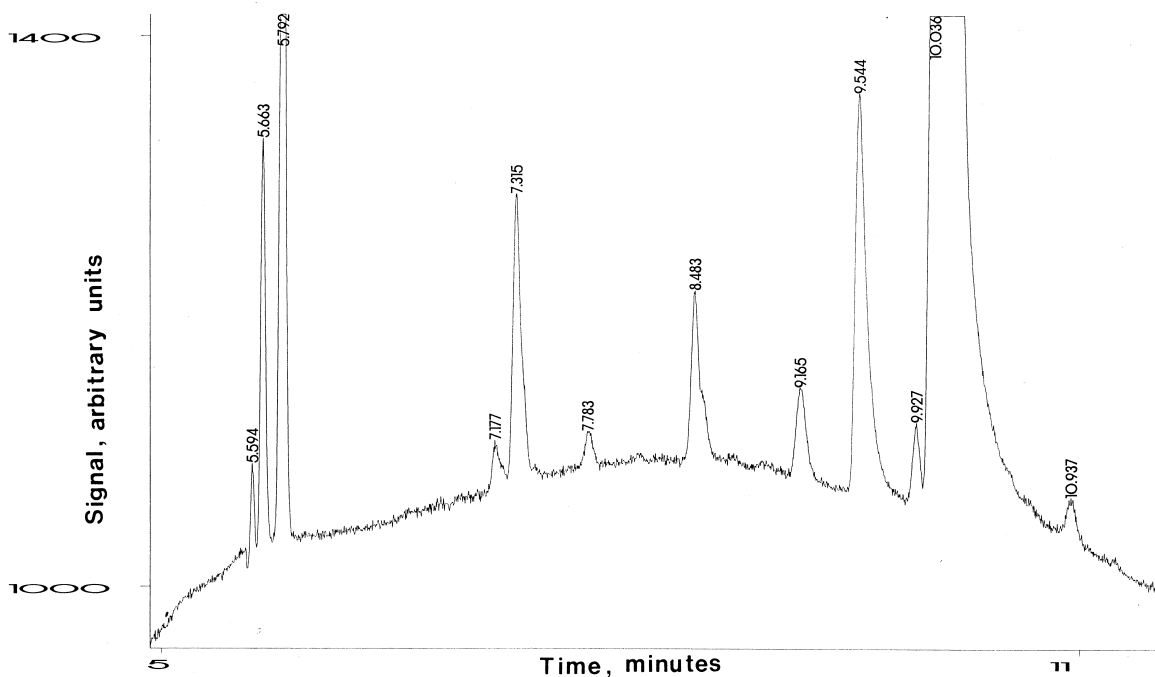


Fig. 4. Relevant portion of ambient air chromatogram, obtained after cryoconcentration on the Carbotrap/glass beads cryo-1. The ethane signal increased the most. Elution times: ethene: 5.594, acetylene: 5.663, ethane: 5.792, propene: 7.177, propane: 7.315, isobutane: 9.165, isobutene and butene-1: 9.927, *n*-butane: 10.036, *cis*-butene-2: 10.937. A Nafion dryer was used for the removal of moisture from a 1.5-l sample of the same air as Fig. 3.

The results of variation of desorption temperature and flow-rates for the glass beads and the Carbotrap/glass beads cryotrap for *o*-xylene are shown in Figs. 5 and 6, respectively. Fig. 5 shows that the desorption of *o*-xylene from the glass beads cryo-1, is quantitative even at the lowest studied temperature and desorption flow-rates. The recovery ranged from 89–93%. The results from the Carbotrap/glass beads cryotrap, shown in Fig. 6, indicate an increase of the desorbed amount of *o*-xylene, with increasing desorption (transfer) time at all studied temperatures. Fig. 6 also shows that the temperature variations did not have any effect on the amount of desorbed *o*-xylene. Maybe the here employed temperature variations were too small to show an effect. Comparing Figs. 5 and 6, the different values obtained from the two examined traps, at the respective conditions, become apparent. These differences would not have occurred if the desorption efficiency were the same for both traps, because always the same amount of *o*-xylene was used.

The desorption performance of the Carbotrap/glass beads vs. the glass beads only trap, was calculated by dividing the mean value obtained for this trap at each set of conditions with the respective value of the glass beads trap. The results are shown in Table 1. The recovery with Carbotrap/glass beads trap was 22–46% less than the recovery with the glass beads only trap. To verify the poorer desorption ability for *o*-xylene of the trap containing Carbotrap, a blank run (in essence a second desorption run without the introduction of sample) was carried out, immediately after the initial desorption. An *o*-xylene peak was always observed, of magnitude larger for the smaller desorption times. The sum of the peak areas of *o*-xylene of the initial (first) desorption plus the additional blank runs was equal to the peak areas observed with the glass beads cryotrap. Up to three blank runs were necessary in order to obtain *o*-xylene peak areas with values less than 0.01 of the total *o*-xylene peak area obtained with the glass beads.

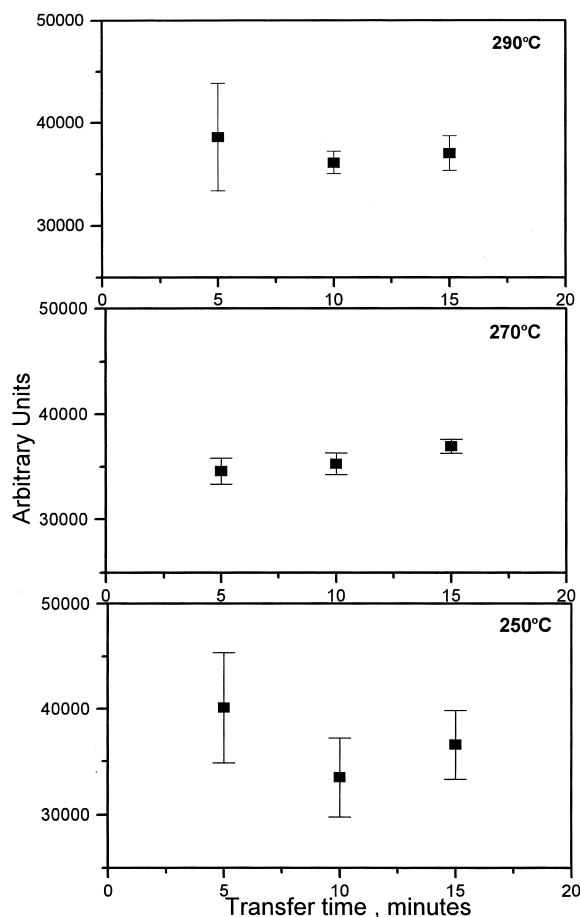


Fig. 5. Effect of variation of transfer time on the obtained detectors signal at the three studied temperatures of the glass beads cryo-1 for *o*-xylene.

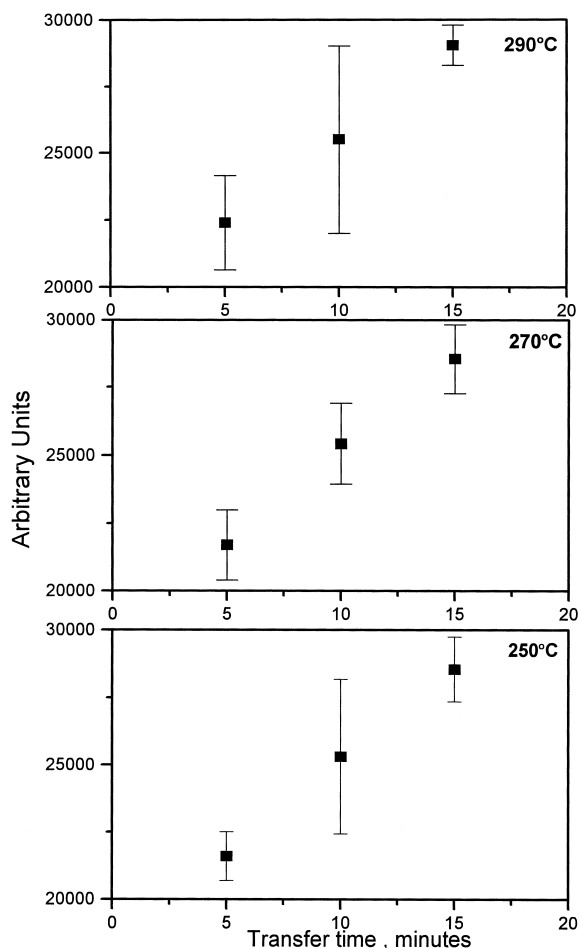


Fig. 6. Effect of variation of transfer time on the obtained detectors signal at the three studied temperatures of the Carbotrap/glass beads cryo-1 for *o*-xylene.

The results presented here on the desorption of *o*-xylene from the Carbotrap/glass beads trap can be compared with the results of Cao and Hewitt [12]. They reported 100% recovery and desorption efficiency of *o*-xylene from a trap filled with Carbotrap at 280°C, desorption time 8 min at desorbing gas flow-rate 35 ml/min. However, the two results may not be so contrasting, since they differ in the desorbing gas flow-rate: ours was 1.5 ml/min to their 35 ml/min. In addition our reported desorption efficiency is equated to the procedure's recovery. Using the desorption efficiency formula of Cao and

Hewitt [12] the calculation with our data at 290°C and desorption time 15 min yields a desorption efficiency of 85%, very close to the results of Cao and Hewitt [12]. Cao and Hewitt's [12] in addition to other studies [13,14] which found that the pinenes are thermally destroyed on the Carbotrap are in contrast to the results of the work carried out in BEMA project, where it was shown that Tenax and Carbotrap yielded the same results for terpene concentration [15]. Our results indicated some destruction of α - and β -pinenes when Carbotrap was used in

Table 1
Variation of the desorption of *o*-xylene from a glass beads and a Carbotrap/glass beads cryotrap

Transfer temperature (°C)	Transfer time (min)	Carbotrap/glass beads mean value	Glass beads mean value	Ratio values (Carbotrap/glass beads) glass beads
290	5	22 401	38 620	0.58
	10	25 518	36 119	0.71
	15	29 050	37 028	0.78
270	5	21 706	34 590	0.63
	10	25 429	35 287	0.72
	15	28 550	36 952	0.77
250	5	21 599	40 128	0.54
	10	25 310	33 519	0.76
	15	28 552	36 597	0.78

the concentration trap. However, field measurements reported pinene concentrations when Carbotrap was used in the adsorbents [1,16].

4. Conclusions

Substitution of some of glass beads of a cryotrap with Carbotrap increased the retention of the C₂ hydrocarbons. Despite the improvement, very low recoveries were achieved for ethylene, which are not satisfactory for ambient air cryoconcentration. Ethane and acetylene were retained more significantly. Both these compounds yielded recoveries around 30% and thus these traps offer greater sensitivity when used in ambient air sampling. The addition, however, of Carbotrap decreased the desorption efficiency of *o*-xylene resulting in a 22–46% lower recovery under all employed conditions. Thus, caution must be exercised in the selection of the desorption conditions when Carbotrap is used in the cryotrap.

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